



FEDERAL REPUBLIC OF GERMANY

1

Issued on  
27 December 1956

GERMAN PATENT OFFICE  
PATENT TEXT

No. 955 094  
CLASS 39B GROUP 22 04  
INTERNAT. CLASS C80G  
F 16475 IV b/39b

RECEIVED  
FEB - 4 2002  
TG 1700

Dr Erwin Windemuth, Leverkusen-Bayer plant

Dr. Fritz Ballauf, Köln-Holweide

and Dr. Dr. h.c. Dr. E.H. Otto Bayer, Leverkusen Bayer plant  
are named as inventors.

Paint Manufacturers Bayer AG, Leverkusen-Bayerwerk

**Process to manufacture surface images from polyisocyanates  
and compounds with more than one reactive hydrogen atom**

Patented in the area of Federal Republic of Germany on 31 December 1954,  
published for patent registration on 6 July 1956  
Patent award declared on 4 December 1956.

There is already a proposal for manufacturing surface images largely resistant to the effect of light, such as films, foils, paint coats, stickers, laminates or preparations of carrier materials by the diisocyanate polyaddition method (periodical Applied Chemistry A.59, 117 [1947]). Besides aliphatic or hydro aromatic polyisocyanates, diphenyl dialkyl methane-4-4'-diisocyanates, 1-alkyl-aryl-2,6-diisocyanates or 1,3,5-triethyl-2,4,6-triisocyanates have been used as isocyanate components.

It has now been found that it is possible to obtain surface images highly resistant to light from organic compounds with more than one reactive hydrogen atom by the isocyanate poly addition method, if tetraalkylated 1,4- or 1,3 phenylene diisocyanates, their free conversion products containing free isocyanate groups with a shortfall of compounds, which contain more than one reactive hydrogen atom, or such conversion products of these isocyanates, in which the isocyanate groups become effective only at raised temperature are used as counter-components for this purpose.

This is a surprising fact and could not be foreseen, because the relevant non-alkylated phenylene diisocyanates deliver surface images tending heavily to yellow.

The high degree of alkylation as well as the type of the substituents of the peralkylated 1'-4 or 1,3-phenylene diisocyanates decides largely the reactivity of the individual types. A weakening in the reactivity desired in comparison with the non-substituted phenylene diisocyanate can be observed in most application areas. The above-mentioned peralkylated phenylene isocyanates do not show any perceivable tendency to secondary reactions, in particular polymerization reactions. This characteristic is manifest in the fact that these isocyanates can be obtained over a long time, even in the form of their conversion products containing their isocyanates. The diisocyanates are obtainable (due to) phosgenization of the corresponding diamines, such as from 2,3,5,6-tetramethyl, 4,6-dimethyl, 3,5-diethyl-, 2,5-dimethyl-3,6-diethyl or the 2,3,5,6-tetraethyl phenyl diamine.

The above-mentioned diisocyanates can be used as such for manufacturing surface images. In many cases, it is advantageous to proceed by way of the low or high molecular isocyanates-containing conversion products of the diisocyanates with a shortfall in compounds, which contain more than one reactive hydrogen atom. To convert suitable compounds, for example, poly-functional alcohols, amines or oxy-amines such as trimethylol propane, glycerin, triethanol amine, diethylene glycol, di-ethanolamine, methyl di-ethanol amine, linear or branched polyester, such as from adipic acid, di-ethylene glycol and/or trimethylol propane with preferably terminal hydroxyl groups, polyester amides, linear or branched polyalkyl ether, such as are obtained through poly-addition of alkylene oxides on poly-functional alcohols. Other technically valuable variants are obtained, if the compounds of the above-mentioned material classes still contain tertiary nitrogen atoms or polymerizable double compounds in the molecule at the same time.

The compounds, which are used as counter-components for the said diisocyanates or their isocyanate-containing conversion products during the manufacture of surface images, should contain more than one reactive hydrogen atom. Particularly suitable are linear or branched condensation products of alkyd resin type, known in the literature under the name "Desmorphene" (ref. "Colors, paints, coating materials 2, 123 [1948]), manufactured from di- and/or polycarboxylic acid and di- and/or polyalcohols. But such modified alkyd resins, for example such as the ones obtainable on using saturated or unsaturated fatty

acids, hydration products of ethylene carbon monoxide mixed polymerisates or epoxy resins, can be used successfully together with the claimed diisocyanates. Furthermore, such classes of substances have proved to be usable, which can be manufactured using the claimed diisocyanates, for example linear or branched condensation products with hydroxyl terminal groups, manufactured from linear or branched polyesters and the said diisocyanates. Of course, high value surface images can be manufactured even with certain simple compounds such as water, bi- or poly-functional alcohols, amines, carboxylic acid amines or carboxylic acid hydrazides. Low or high molecular isocyanate-containing conversion products of the isocyanates with a shortfall of compounds, which contain more than one reactive hydrogen atom, are also advantageously used as poly-isocyanate components.

Diisocyanates are reactive products, which allow manufacture of surface images with high characteristics at room temperature within a technically appropriate period. In cases where the alkyl groups contain more than 1 C atom, for example in tetraethyl or tetra-isopropyl phenylene diisocyanate, the use of higher temperature is however more advisable for conversion to obtain high value surface images.

The measures for reaction acceleration through activators or reaction inhibition through delayers known in isocyanate reactions can also be used equally well in manufacturing the process products. Similarly, use of additives such as fillers, organic or inorganic pigments, metal powders, dyestuffs, softeners etc. can be made in a similar manner. Likewise, use of solvents indifferent to isocyanates in the manufacture of process products is often advantageous.

Further, even such conversion products of the said diisocyanates can be put to use, in which the isocyanate groups become effective only on using high temperatures. Such compounds are obtained, for example by conversion of the diisocyanates with phenols or compounds with active methyl groups such as malonic acid diethyl ester.

The parts listed in the following examples are parts by weight.

### Example 1

48 parts of tetra-ethyl-p-phenylene diisocyanate are added to 100 parts of a 60% solution in ethyl acetate of a polyoxy-compound with an acid number of 0.7 and a hydroxyl content of 10.1% obtained from 810 parts of phthalic acid anhydride, 432 parts of diethylene glycol and 732 parts of trimethylol propane. Films produced by this mixture at a moderately high temperature show

48 Jules  
60 polyester

do not show any yellowing after illumination to light of a carbon arc lamp for several days or to sunlight for several weeks.

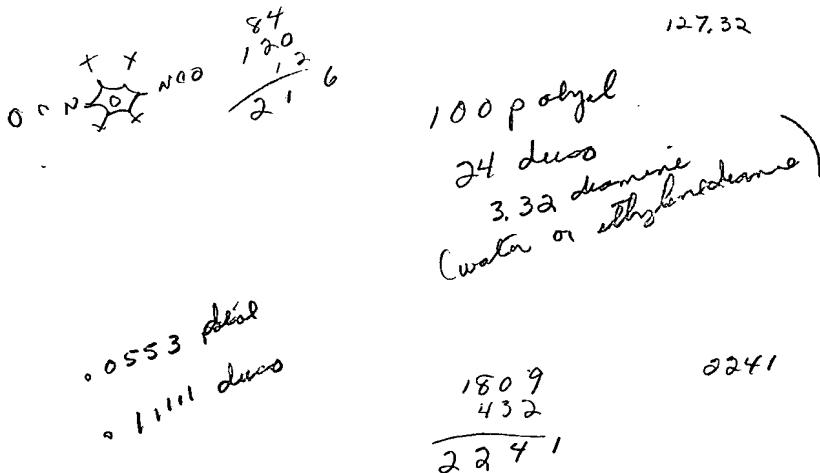
Similarly light-resistant films are obtained, if instead of the pure diisocyanate, 150 parts of 75% solution on ethyl acetate of a conversion product obtained from 1 mol trimethylol propane and 3 mol tetraethyl-p-phenylene isocyanate are made to react with 13.25% NCO, calculated on solid substance.

Even with oil-modified polyoxy-compounds, light-resistant films are obtained, for example one such from 230 parts synthetic fatty acids with 9 to 11 C atoms in the hydrocarbon chain, 283 parts of phthalic acid anhydride, 105 parts trimethylol propane with a hydroxyl content of 5% on reaction with tetraethyl-p-phenylene diisocyanate in a quantity equivalent to the hydroxyl content.

### Example 2

*1809 mol wt*  
78.5% poly<sub>1</sub> 100 parts of a polyester obtained from adipic acid and diethylene glycol with a molecular weight of 1800, 18.9% diiso<sub>2</sub> a QH number of 62 and an acid number smaller than 1 are brought to conversion with 24 parts of tetraethyl-p-phenylene diisocyanate by heating for two hours at 120 to 130°C. The mass obtained, viscous at room temperature, has an NCO content of 3.7%. If this is applied to a surface to a polyamide fabric in a thin layer by means of a painting machine and if such a coated fabric is guided through a gas atmosphere charged with ethylene diamine vapor, a flexible surface image, insoluble in usual organic solvents is obtained on the polyamide web in a reaction occurring within seconds.

On carrying out this coating operation several times for a coat of 50 g/m<sup>2</sup>, a fabric water-proof coated on one-sided is obtained, which shows no yellowing in sunlight and which is ideally suitable for



manufacturing weatherproof clothing.

### Example 3

The isocyanate modified polyester as per the example 2 is used, as mentioned there, for coating a fabric and this fabric is brought into an ager, in which water vapor is present together with vapors of hexahydrodromethylaniline as catalyst.

After subjecting to action by water vapor for 24 hours, a flexible rubbery film has formed from a formerly adhesive coating, with similar properties as in the interlacing with ethylene diamine as per example 2.

## PATENT CLAIMS

1. Process for manufacturing surface images from polyisocyanates and compounds with more than one reactive hydrogen atoms, characterized in that tetraalkyl-1,4- and/or 1,3-phenylenediisocyanates are used as polyisocyanates.
2. Process as per claim 1, characterized in that the diisocyanates are used in the form of low or high molecular isocyanate-containing conversion products with a shortfall of compounds, which contain more than one reactive hydrogen atom.
3. Process as per claim 1, characterized in that the diisocyanates are used in the form of conversion products, in which the isocyanate groups become effective only at higher temperatures.